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Theoretical Studies of Interactions Between TATB Molecules and the Origins of Anisotropic Thermal Expansion and Growth

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Abstract

TATB containing explosives tend to permanently expand as their temperatures are increased or thermally cycled, a phenomenon known as “ratchet-growth.” Several mechanisms as to the cause of the non-reversible growth have been proposed, and are taken up here using various different modeling techniques. High-level quantum chemistry calculations have been used in parameterization of a classical potential function suitable for atomistic simulations of TATB. The quantum-chemistry-based force field for TATB was validated by comparing condensed phase properties obtained from molecular dynamics simulations with available experimental data. No permanent growth was manifest at the molecular level. Dissipative particle dynamics simulations were carried out in order to study the geometric packing effects on the mesoscopic scale, similar to the scales representative of Ultrafine. No permanent growth was identified when only simple packing effects were considered in the TATB model. However, non-reversible growth was displayed when crystal fracture capabilities were incorporated in the

model, suggesting that crystal fracture induced by the anisotropic volume expansion of TATB is the root cause for the permanent growth seen in TATB containing explosives.

Introduction

The compound 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) is used extensively as an energetic material in many applications. Its extensive use stems from the fact that it has excellent thermal stability under thermal, impact or shock initiation [1] and is considered to be quite insensitive at densities near its theoretical maximum [2]. However, TATB containing explosives have a peculiar property in that they permanently grow as their temperatures are increased or as they are thermally cycled. This paper focuses on molecular modeling of not only the expansion behavior TATB single crystals, but on permanent growth of compressed bulk TATB powders.

The experimental geometry of TATB has been determined by X-ray analysis by Cady *et al.* [3], and has been used in the development of a reliable set of intermolecular interaction potentials for TATB allowing the study and evaluation of properties from molecules to the condensed phase, which ultimately provide the ability to study more complex mechanisms observed in TATB, such as the permanent growth identified upon thermal cycling. Perhaps the feature most intriguing about TATB is the relatively large interplanar spacing and the fact that the anisotropic thermal expansion is found to be essentially dominated by expansion along the *c* axis of the unit cell (the perpendicular distance between sheets of hydrogen-bonded TATB), and almost nonexistent in along the *a* or *b* axes.

Our goals here are two-fold; first, we hope to develop a “working” atom-atom intermolecular pair potential for TATB to be used in classical molecular dynamics (MD) that effectively captures the anisotropic changes in its thermal expansion behavior since the use of available force fields, both commercial and public domain, fail miserably when applied to TATB in that the initial simulated crystal structures (see section *atomistic TATB simulations*) undergo polymorphic

transitions into polymorphs that coincide with no known crystal structures of TATB within a matter of a few picoseconds. Moreover, the volume-temperature data reveal significant expansion along both the *a* and *b* axes and contraction along the *c* axis, contrary to experiment. Our second goal is to elucidate the mechanism of ratchet-growth resulting from repeated thermal cycling. To that end, we use our newly developed pair potential for TATB to determine whether the permanent growth seen in TATB containing explosives originate at the molecular level or have origins at a more coarse grain level. In order to study TATB's origins of permanent growth on a coarser size scale, we employ the use of a modeling technique known as dissipative particle dynamics (DPD) [4], which is very similar to MD but applied on a supromolecular size scale. The coarse grained dynamics of a system of interacting particle clusters is accomplished by subjecting the particle clusters to a pairwise dissipative and random ("Brownian") forces.

Force Field Development

The development of the TATB intermolecular pair potential was performed using the second-order Møller-Plesset (MP2) [5] perturbation theory approach. Calculations of intermolecular interactions were performed within the 6-311G(d,p) basis set [6], and were carried out using the Gaussian 98 code [7]. The calculations were performed on either of two different TATB dimers; the two closest neighbors along either the *c* (*c*-dimer complex) or *a* (*a*-dimer complex) axis of the TATB unit cell, as shown in [figure 1](#).

The valence terms used to model TATB atomistically consisted of a quartic polynomial for bond stretching and angle bending, a three-term Fourier expansion for torsions and the out-of-plane coordinate is that defined by Wilson *et al.* [8].

Single-point energies were computed for a total of eleven different dimer configurations along both the *c*- and *a*- axes, where each of the different configurations represent changes in distance along each of the corresponding axes, namely, single-point energies were performed at the equilibrium crystal distance (0 Å) as well as ± 0.25 Å, ± 0.5 Å, ± 1.0 Å, ± 1.5 Å, $+2.0$ Å, and $+2.5$ Å. Additionally, each of the dimer configurations were corrected using the Basis Set

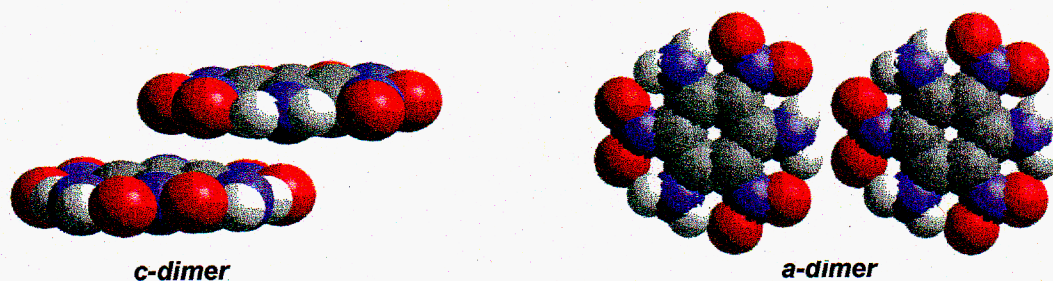


Figure 1: Molecular clusters used in the in determining the interaction energy between TATB dimers along either the *c* (*c-dimer*) or *a* (*a-dimer*) axis of the TATB unit cell.

Superposition Error (BSSE) correction [9] due to the large basis set used. The BSSE corrected interaction energy was then further decomposed into its corresponding atom-atom pair potentials by fitting to a Lennard Jones (LJ) 12-6 type potential functions plus Coulomb for the electrostatic contributions. The charge on each constituent atom in TATB for uses in fitting the Coulombic term in the atom-atom pair potentials was determined using the Merz-Kollman Singh (MK) charge method contained within the Gaussian 98 code [7]. The sum of the LJ contributions to the atom-atom pair potentials fits along with the Coulombic contributions are compared to the BSSE corrected total interaction energies for both the *c*- and *a*-dimer complexes are shown in [figure 2](#). It should be noted that

Computational Details

The modeling methods employed in this work consist of both classical MD and DPD simulation techniques so as to treat both atomistic and supromolecular length size scales.

a. Atomistic TATB Simulations

Using the newly developed TATB atom-atom pair potentials discussed above, we perform MD simulations of fully atomistic TATB. All valence degrees of freedom were explicitly treated and unconstrained. Non-bonded interactions were truncated for atom pairs with an inter-atomic distance greater than 9.5 Å. The

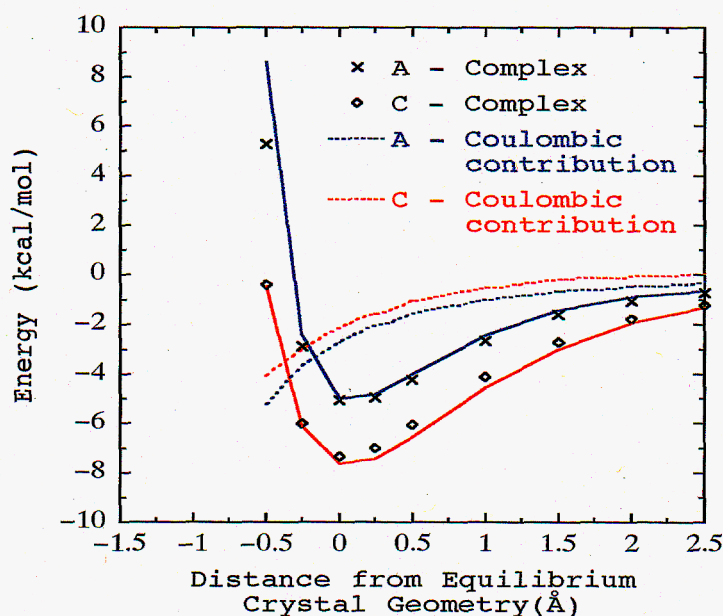


Figure 2: Total BSSE corrected interaction energy along with LJ 12-6 fits and Colombic contributions for both C- and A-dimer complexes.

truncation was implemented using a fifth-order spline between 8.5 Å and 9.5 Å to avoid discontinuities in the energies at the cutoff. A buffer width of 0.5 Å was used in the generation of the neighbor list. The long-range electrostatic interactions were calculated employing the standard Ewald summation techniques [10].

The initial TATB structures used in the simulations were that of Cady *et al.* [3]. The periodic unit cell consisted of 54 TATB molecules. MD simulation data was generated using constant particle number, pressure, and temperature (*NPT*) dynamics at a pressure of 0 atm. The Verlet velocity [10] time integration method was used with a time step of 0.5 fs. The Parrinello-Rahman method of pressure control [11] was used for constant *NPT* dynamics, thus allowing both the size and shape of the simulation cell to dynamically adjust and possible polymorphic transitions of the TATB unit cell. All structures were initially energy minimized before dynamic simulations were performed. The systems were temperature cycled in *NPT* runs starting at 200 K and incrementally increasing the temperature

in steps of the 25 K to a maximum temperature of 375 K and then incrementally cooled using the same approach. The systems were allowed to dynamically evolved at each temperature for a total of 100 ps before the temperature was incremented.

All computations were carried out with the OFF algorithm in the commercial software program from Molecular Simulations, Inc. [12].

Validation of the use of our newly developed force field, herein to be referred to as QMFF (quantum based force field), as a atomistic model for TATB is found by comparing the X-ray powder diffraction (XPD) of our model TATB crystal after heating the initial TATB crystal unit cell from 200 K to 275 K in MD runs using our newly developed force field as detailed above, with the XRD obtained from the experimental crystal structure reported by Cady *et al.* [3] ([figure 3](#)). As is apparent, the agreement between the simulated structure and that of experiment is quite good, where the (002) peak located at $\sim 28^\circ$ differs by less than 0.3° , and may in

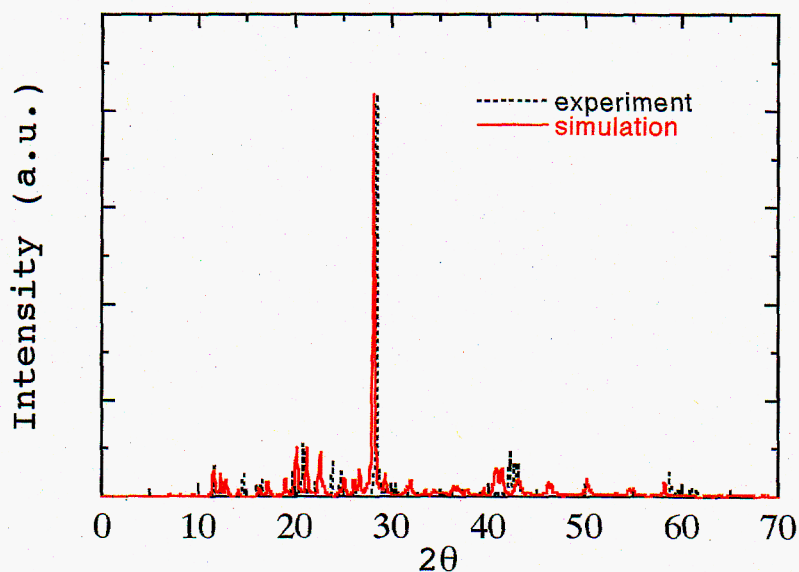


Figure 3: X-ray powder diffraction spectra for TATB: solid curve represents MD simulation results using our QMFF force field; dotted curve is the experimental crystal data of Cady *et al.* [3]

fact be due to shifts to smaller 2θ caused by the higher temperature of the simulation data.

The MD volume-temperature results of the bulk triclinic TATB crystal, obtained using our QMFF force field, is shown in [figure 4](#) along with experimental data of Kolb *et al.* [13]. As is readily apparent, the simulation results compare quite well with experiment over the entire temperature range of 200 K to 375 K. The curves labeled cFF1 and RFF1 represent the CFF91 commercial force field [14,15] where the rotation of the NH_2 and NO_2 moieties have been constrained (cFF1) or where non-bonded interactions between the constituent atoms in the adjacent NH_2 and NO_2 moieties have been disabled (RFF1). The limitations imposed in either of the cFF1 or RFF1 have been imposed so as to eliminate the rapid polymorphic transitions of the crystal structures of TATB mentioned earlier. The curve labeled QMFF represents our newly derived atom-atom pair potentials.

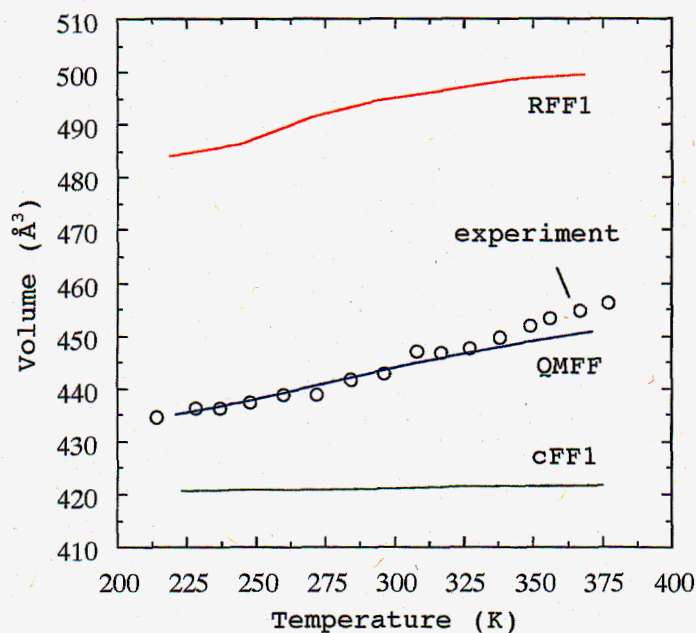


Figure 4: Volume-temperature relation for TATB at 0 atm as determined from *NPT* dynamics. The MD simulation results (solid curves) and experimental values (circles) are both shown.

The thermal expansion behavior of our model TATB crystal is virtually unidimensional expansion of the *c*-axis consistent with experiment, as is the fact that the cell angles remain effectively constant. Perhaps more importantly, at least for the sake of addressing our goals here, is the fact that thermal cycling the crystal exhibits no permanent growth as is found experimentally [13].

b. Mesoscale TATB Model

Because an atomistic origin of permanent growth was not identified, and our goal is to elucidate the origins of such, it therefore necessary to investigate a coarser grained size scale model. It is our hope that a coarser size scale model may allow for direct investigation of the geometrical packing effects on the permanent growth in TATB. As stated earlier, we chose to model this length scale using dissipative particle dynamics. Our DPD model TATB consists of ternary distribution of TATB crystallites composed of 10 - 5x5x5, 3 - 6x6x6, and 2 - 8x8x8 DPD molecular clusters or “beads”, where each spherical bead, having a diameter of 0.02 μm , represents a cluster of TATB molecules ($\sim 4.5 \times 10^9$ TATB molecules), which gives a average crystallite particle size distribution of $\sim 5.6 \mu\text{m}$; similar to that found in Ultrafine. The beads are subjected to pairwise conservative, dissipative and random forces. In this study the conservative interaction potential between the TATB molecular clusters is either an R^{-12} , or a Morse type potential, which provide the ability for crystal fracture within the TATB crystallites. Additionally, the TATB beads are harmonically bound into the corresponding crystallites discussed above, when interacting via the R^{-12} (herein referred to as the “harmonic-model”). When interacting via the Morse potential a gaussian function is coupled to the potential (herein referred to as the “Morse-model”) so as to prevent unphysical fusing of the interacting beads (see [figure 5](#)). The non-bonded interactions were truncated for interacting bead pairs with an inter-atomic distance greater than 0.05 μm . The cell linked-lists method was used in the generation of the neighbor list [10].

In addition to the simulation details described above, the crystallites were made to anisotropically expand by $\sim 4.5 \%$ in the “*c*-axis”. An illustration of the Ultrafine model TATB is shown in [figure 6](#).

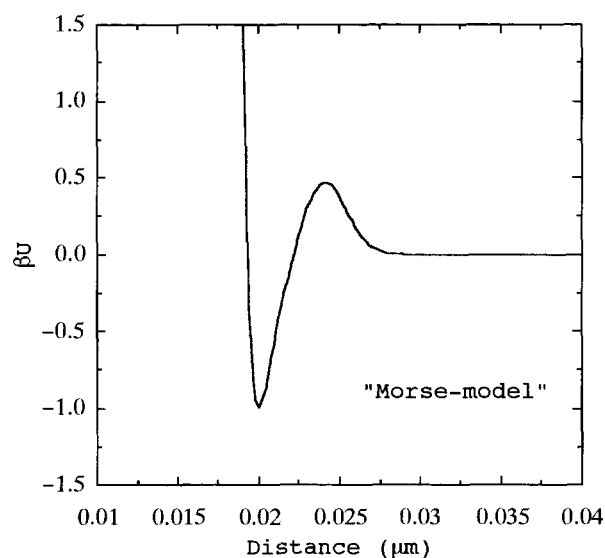


Figure 5: The Morse model conservative pair potential between interacting TATB molecular clusters (beads).

We next present our findings of thermal cycling of the dimensional change of both the harmonic and Morse mesoscale TATB models. The systems were temperature cycled in *NPT* runs starting at 89 K and incrementally increasing the temperature in steps of the 43.5 K to a maximum temperature of either 400.5 K or 356 K, for the harmonic and Morse models, respectively and then incrementally cooled using the same approach. The systems were allowed to dynamically evolved at each temperature for a total of either ~ 4.1 s or ~ 0.25 s before the temperature was incremented, for the harmonic- and Morse-model, respectively. The dimensional change as a function of thermal cycling is shown for the harmonic- (panel *a*) and Morse-model (panel *b*) in [figure 7](#). As is apparent in [figure 7a](#), the harmonic mesoscale TATB model does *not* exhibit and permanent growth upon thermal cycling (two cycles shown here); thus, suggesting that the origins of the permanent growth are *not* a geometrical packing effect. However, when the ability for crystal fracture is incorporated into the model (Morse-model), permanent growth was identified after thermal cycling, as seen in [figure 7b](#). The amount of

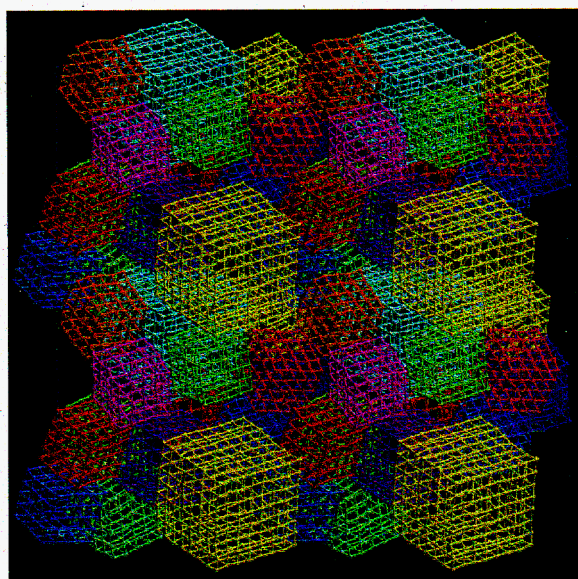


Figure 6: Illustration of the ultrafine mesoscale TATB model consisting of a ternary distribution of TATB crystallites; each spherical bead in the crystallite lattice represents a molecular cluster of $\sim 4.5 \times 10^9$ TATB molecules.

growth exhibited in our model is greater than that found experimentally{Cunningham, 2001 #35} (see inset in [figure 7b](#)), which is due in part to the rapid quench rates the TATB crystallites experience, as well as the height of the fusing barrier (gaussian hump) used in our model. Preliminary results show that better quantitative agreement with the amount of permanent growth displayed in our model TATB may be obtained by increasing the barrier height, additionally, we are using MD to determine an effective potential of mean force between TATB crystallites in hope of determining the height of the barrier to use in our DPD simulations.

The next issue we address is whether the permanent growth exhibited in compressed bulk TATB powders has its origins in the anisotropic expansion found in TATB. To that end, we allow for the individual TATB crystallites in our mesoscale reveal no permanent growth, but rather volumetric shrinkage, suggesting the

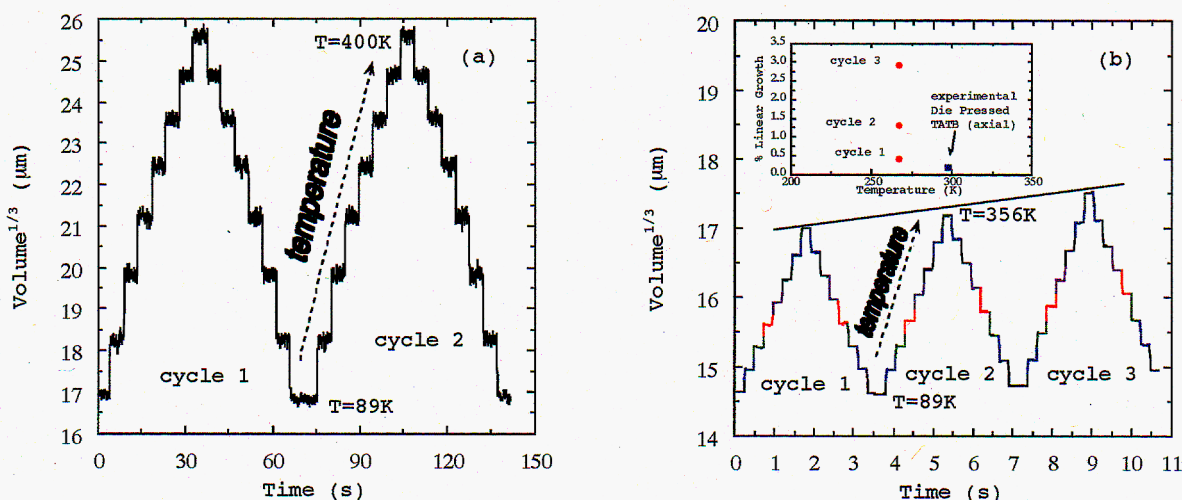


Figure 7: Dimensional change of ultrafine mesoscale TATB model as a function of time: panel *a* and *b* shows the dimensional change for the harmonic- and Morse-model TATB, respectively. The temperature is incrementally changed from 89 K to 400 K over time. The insert if panel *b* compares the total linear growth of our simulations to experiment.

TATB model to isotropically expand as the temperature is cycled. The simulations anisotropic expansion of TATB as an integral detail in the growth mechanism.

The final issue we address is whether the permanent growth exhibited in compressed bulk TATB powders has its origins in the anisotropic expansion found in TATB. To that end, we allow for the individual TATB crystallites in our mesoscale TATB model to isotropically expand as the temperature is cycled. The simulations reveal no permanent growth, but rather volumetric shrinkage, suggesting the anisotropic expansion of TATB as an integral detail in the growth mechanism.

Conclusions

The focus of this article is on the origins of permanent growth in TATB containing explosives. We have developed a quantum mechanical force field for atomistic simulations of TATB that successfully describes the anisotropic behavior of TATB over a wide temperature range. Our newly developed TATB model, when applied to bulk single TATB crystals, indicate no permanent expansion at the

molecular level, consistent with experiment. Further, our investigations of the expansion properties of bulk pressed TATB powders also display no permanent expansion when only geometric packing is considered. However, when the ability for crystal fracture is incorporated into the model permanent expansion is in fact identified. The view that crystal fracture, induced by stresses within the bulk material upon thermal cycling, and the difference in rates of expansion between the individual crystallites in the bulk material and the entire body of crystallites in the entire bulk material, is one of the potential causes of the permanent growth seen in crystalline bulk pressed powders has been suggested by Naum [16] *et al.* and is the view taken up here. Finally, we believe that the anisotropic expansion of TATB to be one of the root causes of the stress experience within the pressed bulk powders, thus leading to crystal fracture and ultimately permanent growth upon thermal cycling.

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